Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 55 (2014) 503 – 511

Physics Procedia

Eighth International Conference on Material Sciences, CSM8-ISM5

Study of the photo-oxidation and photolysis of unsaturated and cross-linked polyesters (UP) in the presence of photoactive or not inorganic fillers

Zahi KHALIL[*1], Bachar KOUBAISSY[2,3], Mariam AKIL[2]

1. *Laboratoire de Photochimie Moléculaire et Macromoléculaire de l'Université de Clermont II- Ensemble Universitaire de Cézeaux, 63177 Aubière Cedex France*
2. *Lebanese university, Faculty of sciences section V, Nabatieh, Lebanon*
3. *Laboratory of Materials, Catalysis, Environment and Analytical Methods, Faculty of Sciences I, Lebanese University, Campus Rafic Hariri, Beyrouth, Lebanon*

Abstract

Disturbances of the photochemical evolution involved in the photolysis and in the photo-oxidation at long wavelengths (λ≥300 nm) of poly(propylene glycol-maleatophtalate cross-linked by the styrene (UP) ,caused by the addition of photo-active pigment such as zinc sulphide or black iron oxides ,and no photoactive inorganic fillers such as calcium carbonate have been analysed by means of FTIR and U.V. spectrophotometry.

The photo-oxidation observed by FTIR of the polymer UP in the presence of inorganic fillers leads to the same photoproducts such as ones of the photo-oxidation of the virgin polymer, but the oxidation rate is greatly affected by the nature and the percentage of the inorganic filler. Zinc sulfide and black iron are incorporated in the film of polymers, the absorption spectra of ZnS reveals that this pigment is not as absorbent as titanium oxide in a more limited field. On the other hand, with a very low inner filter effect, black iron oxides promote the formation of absorbing photoproducts. The addition of Calcium carbonate non- absorbing filler to the UP, causes a slight decrease in the evolution of the I.R

Peer-review under responsibility of the Organizing Committee of CSM8-ISM5

Keywords: polyesters, Zinc sulphide , black Iron Oxides, Calcium Carbonate, pigment,photo-oxidation, Photolysis.

1. Introduction

Numerous coating systems based on epoxy and unsaturated polyester (UP) resins are available for industrial and submerged structures, but they are not completely satisfactory from the viewpoint of prevention of corrosion and fouling (Anand Prabu et al, 2004).

E.mail address: zahi.khalil@hotmail.com,

Peer-review under responsibility of the Organizing Committee of CSM8-ISM5
doi:10.1016/j.phpro.2014.07.075

The inorganic fillers which are introduced in the polymeric materials can be either absorbent, such as photoactive pigments (Pan et al, 2007; Jia et al, 2008) or non-absorbent such as calcium carbonate (Avolio et al, 2013; Mòczò et al, 2002) or alumina "tri-hydrate. (Joni et al, 2010; Gao et al, 2005). The introduction of absorbent loads present on the fundamental level, an essential interest, they cause disturbances that are often used to analyse the mechanism of photo-oxidation of polymers.
In the category of concerned photo catalysts zinc oxide (ZnO), titanium dioxide (TiO_2) has been widely investigated (Parida et al, 2006; Pardeshi et al, 2008). These studies are for photocatalytic degradation of organic pollutants in waste water treatment. However, photocatalytic activity of zinc sulphde nanoparticles (ZnS NPs) has not been studied in detail because of some limitations (Gou et al., 2004; Kohtani et al., 2005; Zhang et al., 2007a,b). For the photocatalytic degradation of organic pollutants such as dyes existence of electron–hole pair at the surface is needed (Zhang et al., 2007a,b).
Indeed, the excitement of a photoactive pigment causes the formation of active species likely to initiate photo-oxidation reactions in the polymer (O_2* ($^1\Delta g$), $O^{\bullet}_{(ads)}$, $O^{\bullet}*_{(ads)}$, $OH^{\bullet}$, $OH^{\bullet}_2$) (Lee et al, 2006; Snider et al, 2010). Currently, no definitive mechanism of production of excited species can be retained; there is no data on the energy of the different chemisorbed species phase. Among the cited species, most authors retain per-hydroxyl and hydroxyl radicals $OH^{\bullet}$ and $OH^{\bullet}_2$ as responsible for most of photo-catalytic phenomena.
The overall effect of a pigment pro-oxidant or stabilizer depends on the polymer base percentage and pigment dispersion in matrix. Inner filter effects and photo-catalysis will compete and only the experience will give us information on the preponderant phenomenon.

2. Experimental Method

We have examined the cross-linked unsaturated polyesters "UP" which are mainly polymers of the class of thermosets, whose implementation leads to cross-linked materials. They are very easy to build by charges and glass fibber. They are very appreciated for their flexibility of implementation and their properties: These materials can compete with metals in several areas and especially in the transportation industries.
The development of cross-linked and unsaturated polyester involves two steps (Lemaire et al, 1979 and 1981):
- A poly-esterification between di-acids (isophthalic acid / maleic anhydride) and glycols (1,2 propylene glycol)
- A radical copolymerization with styrene (Weiss et al, 1983)
Samples of polymer (UP) were provided as homogeneous film of variable thickness, and the incorporated fillers are :

a. Photo-active: -Zinc Sulphide and Black Iron Oxides.

With Zinc Sulphide, two types of mixtures have been realized containing either 2.5% or 10%. The content of black oxide of iron is 0.5%, 1%, 2.5%, 5%. For such pigment concentrations, we examined using a UV spectrophotometer equipped with an integrating absorption sphere spectra and the results are presented in the table1:

Table 1. Different mixtures of polyesters prepared and their properties

Mixture (e=110 μm)	absorption domain of photons by the pigment	Optical density at 325 nm (2.5% of pigment)	Scattered light and backscattered at λ >
A + ZnS	300-340 nm	1.2	340 nm
A + black iron oxides	300-800 nm	0.6	310 nm

b. Non photo-active: Calcium carbonate.

Calcium Carbonate is an original calcite Urgonian very high chemical purity "Millicarb", characterized by a diameter of three microns approximately.
Four type of mixture were carried out with 10%, 30%, 50% and 100%.

The study of the evolution of the material required the use of multiple irradiation and analysis equipment:

Irradiation conditions

• A long-wavelength: polychromatic irradiation apparatus called SEPAP 12-24, consists of four mercury vapour lamps "medium pressure", type MY MAZDA 400 W, allows only radiation of wavelength greater than 300 nm. The central portion of the chamber, located 25 cm from the lamps, is equipped with a turret samples (24) animated by a circular and uniform movement. The temperature is controlled continuously by a thermocouple contact and stabilized at 2 ° C between 40°C and 80 °C.
• A short wavelength irradiation apparatus SEPAP 254 consists of a cylindrical reflector agents based elliptic. The source, a monochromatic tube mercury vapour "low pressure" emitting at 253.7 nm, embodies one of its focal axes. The other focal axis coincides with the axis of a sample turret (24) driven in a uniform movement of rotation. Irradiation was performed at room temperature.

Analysis

Changings in chemical structure of polymers is examined by UV analysis on a Perkin Elmer 554 equipped with an integrating sphere, or I.R on a Perkin Elmer 682 spectrophotometer and a FTIR Nicolet 20 SX.

Titration of hydro-peroxides

The determination of hydro-peroxides is performed according to the method described by Petruj et al (Petruj et al, 1980) which is based on the ambient temperature oxidation of Fe^{2+} and the formation of a complex between Fe^{3+} and SCN^- ions.

3. Results

3.1. Study of the photo-oxidation of the polymer UP pigmented with Zinc Sulphide:

Pigmented samples of polymer UP with 2.5% and 10% Zinc Sulphide are irradiated in a chamber SEPAP 12-24 at 60 °C. Chemical evolution of these samples was examined by I.R. and U.V. spectrophotometry.

3.1.1. Analysis of photoproducts observed in I.R.

The photo-oxidation of these samples leads to the formation of oxidation photoproducts observed in I.R. We noted mainly the appearance of three bands at 3300, 3400 and 3465 cm^{-1} in the hydroxyls region and the expansion of the initial band in the field of carbonyls. The incorporation of Zinc Sulphide does not modify the evolution of the IR spectrum of virgin polymer during photo-oxidation. There were not a particular important development in the field of hydro-peroxides absorption (3400-3600 cm^{-1}). As Titanium Oxide, Zinc Sulphide does not protect photo-chemically unstable and intermediate products such as hydro-peroxides (Figure 1)

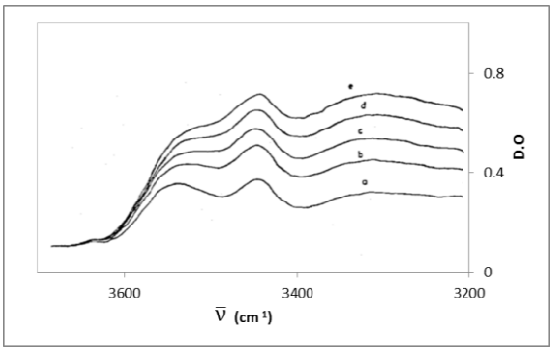
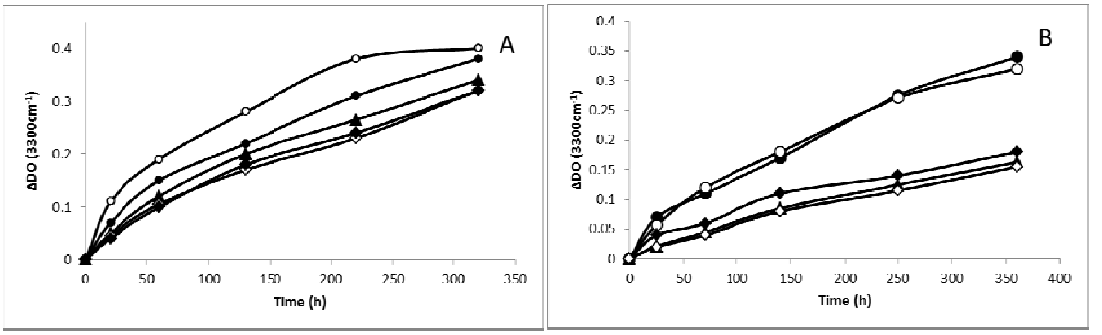


Figure1: Evolution of the IR spectrum of a polymer UP (10% ZnS). (e = 116 µm). a: original, b: 65 h, c: 131 h, d: 221h and e: 314 h

We examined the kinetics of appearance of oxidation photoproducts observed in I.R. As shown in Figure 2, the optical density increases rapidly at the beginning of irradiation, and then varies linearly with irradiation time. The comparison of the evolution of the IR spectrum of virgin and pigmented samples shows that the introduction of Zinc Sulphide with low rate (+2.5%) (Fig. 2-A) in the polymer increases the rate of formation of photo-oxidation products. At high rate (+10%) (Figure 2-B), we find that the rate of photo-oxidation of pigmented polymer is identical to that one of the virgin polymer .Moreover, if we compare, with identical content (2.5%), the evolution of I.R. spectra of samples pigmented with Zinc Sulphide to that pigmented ones with Titanium oxides, the acceleration of the oxidation caused by the Zinc Sulphide is more important.



Figures 2: increase in optical density at 3300 cm^{-1} of a pigmented polymer UP, versus the duration of irradiation. (e = 120 microns) A : (+ 2.5% pigment) , B :(+ 10 % pigment). (●): Virgin, (○): +ZnS, (▲): +TiO_2 rutile I. (♦) :TiO_2 anatase and (◊): TiO_2 rutile II.

3.1.2. Analysis of photoproducts absorbing U.V.

The U.V. spectra analysis shows that the U.V. photo-oxidation of samples pigmented with Zinc Sulphide causes the formation of absorbent photoproducts. The evolution of the UV spectrum is observed between 350-500 nm with 10 % ZnS (Figure 3-A), and with 2.5 % ZnS (Figure 3-B). The examination of U.V. spectra shows a significant increases of the rate of formation of photoproducts in the presence of Zinc Sulphide, and the optical density increases faster when the rate is low (2.5%). Finally, if we compare the evolution of the UV spectra of pigmented samples with TiO_2 and ZnS, at the same rate, we noted that the variations in the optical density of samples pigmented with ZnS are greater.

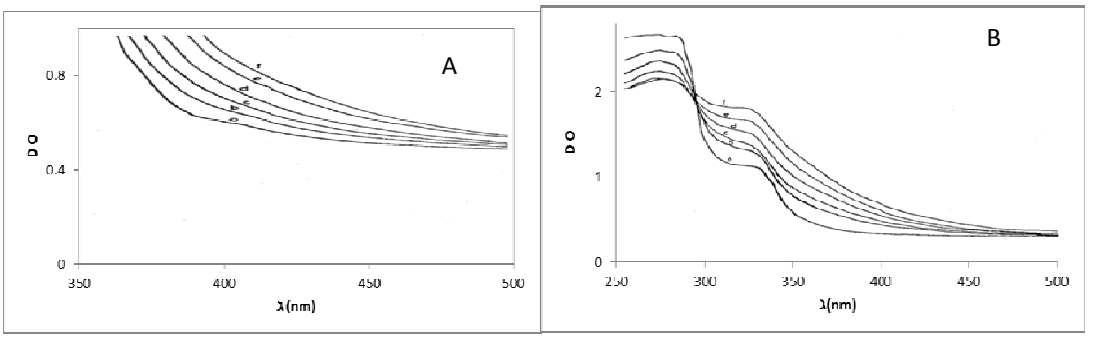


Figure 3: Evolution of the UV spectrum of a polymer UP: A (UP + 10% ZnS, e = 116 microns) , B (UP + 2.5 % ZnS , e = 110 microns). a: original, b: 25 h, c: 65 h, d: 131h, e: 221 h, f: 314 h

3.2. Study of the photo-oxidation of polymer UP pigmented with Black Iron Oxides

The influence of black iron oxides on the photo-oxidation of the polymer UP was examined. Four types of mixtures prepared with 0.5%, 1%, 2.5% and 5% of pigment were irradiated in the enclosure SEPAP 12-24 at 60°C .The chemical evolution of these samples is followed by I.R. and U.V. spectrophotometry.

3.2.1. Analysis of photoproducts absorbing in I.R.:

The evolution of I.R. spectra of irradiated samples, analogous to that one of virgin polymer, is characterized by the increase in optical density in the field of hydroxyls (Figure 4-B) and the enlargement of the initial band in the field of carbonyls. If we examine the kinetics of formation of observed photoproducts, we find that the incorporation of black iron oxides in the polymer UP increases the rate of oxidation of the polymer. As shown in (Figure 5-B), changings in optical density are practically equivalent for the samples with 0.5%, 1%, 2.5% of iron oxide, but decrease for pigmented samples with 5% black iron oxides.

3.2.2. Analysis of photoproducts absorbing in U.V:

The evolution of U.V. spectra of samples pigmented with iron oxides is similar to that of the virgin polymer. On observed an increase in density between 300-500 nm reflecting the formation of highly absorbent photoproducts (Figure 4-A) .Looking at the evolution of the UV spectrum regarding to the rate of introduced oxides, we see that the kinetics of appearance of absorbing photoproducts is different from that one of virgin polymer; the photo-oxidation is self-accelerating (Figure 5-A). The introduction of iron oxide black in the polymer increases UP significantly the rate of formation of absorbing photoproducts. This increase is even as more important as the iron oxides content is higher.

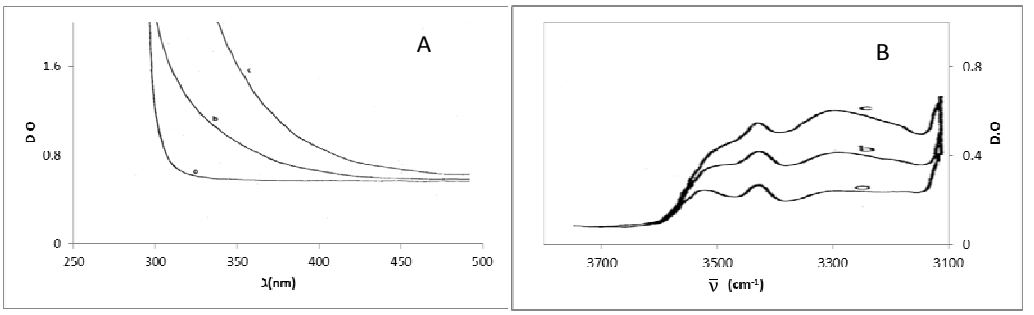


Figure 4: evolution of UV spectrum (A) and IR (B) of a polymer UP (+ 1% black iron oxide). (e = 94 microns). a: original, b: 63 h, c: 130 .

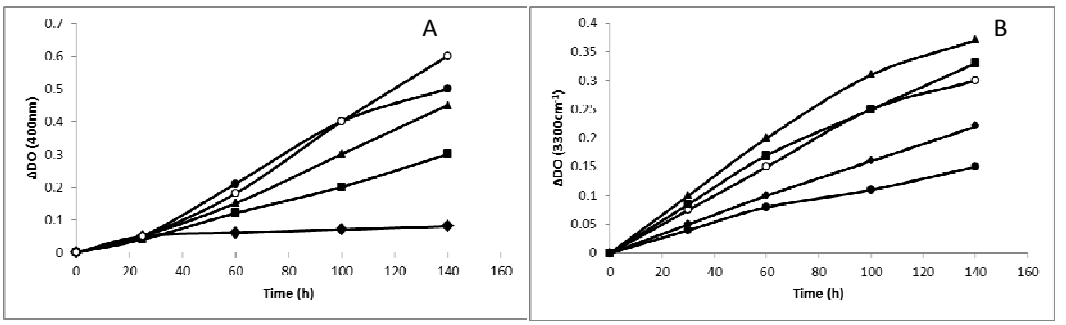


Figure 5: increase of optical density at 400 nm (A) and at 3300 cm^{-1} (B) ,of samples UP + black iron oxides versus the duration of irradiation (e = 100 microns). (♦): virgin, (■): 0.5%, (▲):1%, (○): 2.5% and (●): 5%

3.3. Study of the effect of Calcium carbonate on the photo-oxidation of polymer

Calcium carbonate is a inorganic filler photo-chemically neutral (Fanton et al, 1983) with density of 2.7 to 2.8. Its introduction into polymeric materials has proven to be an interesting technic. In industry the reduction of the cost of final mixtures without affecting their mechanical properties is very important. Sometimes calcium carbonate is used to achieve a better distribution of additives within the material.

The influence of calcium carbonate on chemical evolution of the polymer UP during photo-oxidation was examined.

3.3.1. Analysis of oxidation photoproducts observed in IR:

The analysis of IR spectra shows that the introduction of calcium carbonate in the polymer UP does not affect the evolution of IR spectrum. The variations in the field of hydroxyls and carbonyls are all comparable with those of virgin polymer. The kinetic study of the formation of oxidation photoproducts shows that the optical density increases rapidly at the beginning of irradiation, and then varies linearly with exposure time of polymer. The comparison of changings in IR spectra of virgin and mixed samples has required a thickness correction, taking into account the density of the polymer (value taken 1.3), the rate of calcium carbonate and its density. As shown in (Figure 6–A), the introduction of calcium carbonate in the polymer UP causes a slight decrease in the rate of formation of photoproducts observed in IR.

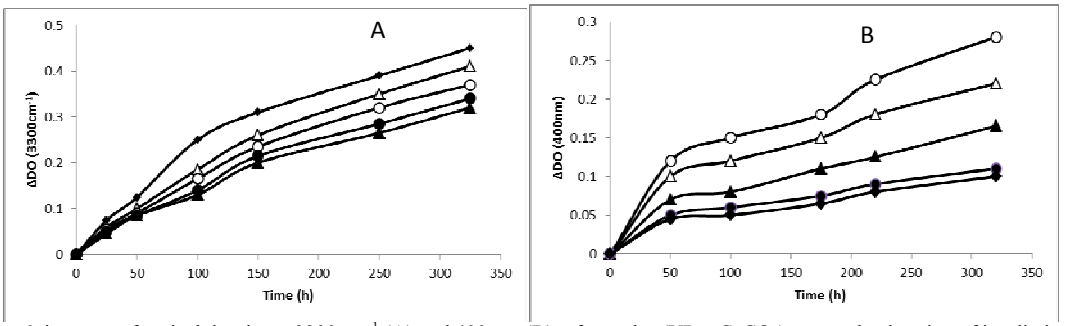


Figure 6: increase of optical density at 3300 cm^{-1} (A) and 400 nm (B) of samples (UP + $CaCO_3$) versus the duration of irradiation. (e = 125 microns). (♦): virgin, (●):10p, (▲) : 30p, (Δ):50p and (○):100p.

3.3.2. Analysis of oxidation photoproducts observed in UV:

The photochemical evolution of samples UP containing various rates of $CaCO_3$ is different compared to that one of the virgin polymer. As shown in (Figure 6–B), the evolution of UV spectra observed between 250-500 nm is more important at long wavelengths when the polymer is prepared with $CaCO_3$, due to the formation of absorbing photoproducts. As shown in (Fig.7) the change of optical density at 400 nm regarding to the irradiation duration is represented. The introduction of calcium carbonate increases the rate of formation of absorbing photoproducts; it is more important as higher as the rate of $CaCO_3$.(Fig.8)

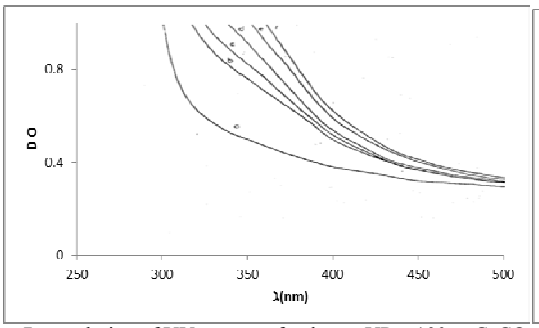


Figure 7: evolution of UV spectra of polymer UP + 100 p $CaCO_3$ irradiated at λ ≥300nm . (e=167 µm) (e=175 µm) a: initial , b: 56 h , c: 99 h , d : 165 h , e: 231 h, f : 323 h.

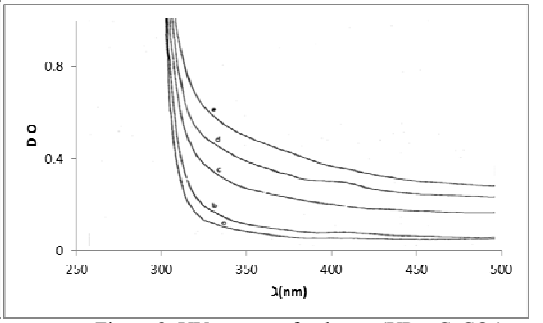


Figure 8: UV spectra of polymer (UP + $CaCO_3$), a:virgin(e =116µm); b: +10p (e =170 µm); c:+30 p d:+50 p (e =168 µm); e: +100 p (e =160 µm).

3. 4. photolysis study of the UP polymer with calcium carbonate

Samples of polymer UP, prepared of 50 parts calcium carbonate to 100 parts of polymer are irradiated under vacuum at wavelengths above 315 nm and at a temperature of 45 ° C. The equivalent thickness loaded samples is equal to that of virgin samples.

3.4.1. Analysis of photoproducts absorbing in I.R.:

The introduction of calcium carbonate in the polymer UP does not affect the evolution of I.R spectra. In the field of hydroxyls, we observe the appearance of a broad band around 3300 cm^{-1} attributed to photolysis products. The kinetic study of the optical density at 3300 cm^{-1}, shows that the rate of formation of photolysis products is not disturbed by the incorporation of calcium carbonate.

3.4.2. Analysis of oxidation photoproducts observed in UV:

The irradiation under vacuum of samples UP with of calcium carbonate leads to a significant changings of optical density between 300-500 nm, due to the formation of very absorbing photolysis products. The comparison of changings of UV spectra between virgin and mixed samples indicates that the incorporation of calcium carbonate in the polymer UP led to more important evolution of optical density in the field of long wavelengths (Figures 9 -10).

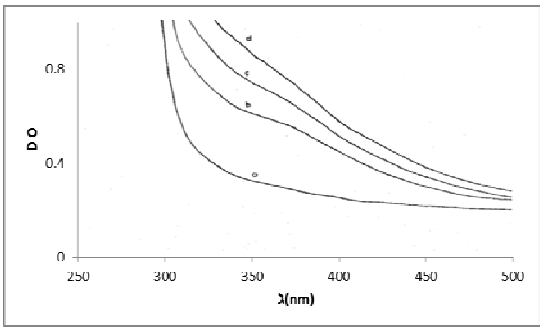


Figure 9: Evolution of UV spectra of polymer UP +50 p $CaCO_3$ Irradiated under vacuum at $\lambda \geq 315$nm. (e = 148 µm).
a: initial , b: 213 h , c: 396 h , d : 604h.

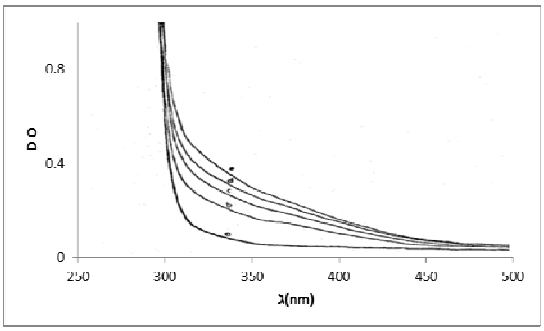


Figure 10: Evolution of UV spectra of virgin polymer (UP) Irradiated under vacuum at $\lambda \geq 315$nm. (e=105µm)
a : initial , b : 94 h , c : 257 h , d : 423 h.

The study of the rate of formation of absorbing photolysis products shows that as per the virgin polymer, some photolysis products have proven unstable in the oxidizing medium. In fact, the photo-oxidation of samples irradiated under vacuum first causes the decrease of the absorbance between 300-500 nm, explained by the transformation of photoproducts in less absorbing ones, but their concentration in samples with $CaCO_3$ is significantly higher than that ones in the virgin polymer (Fig. 11).

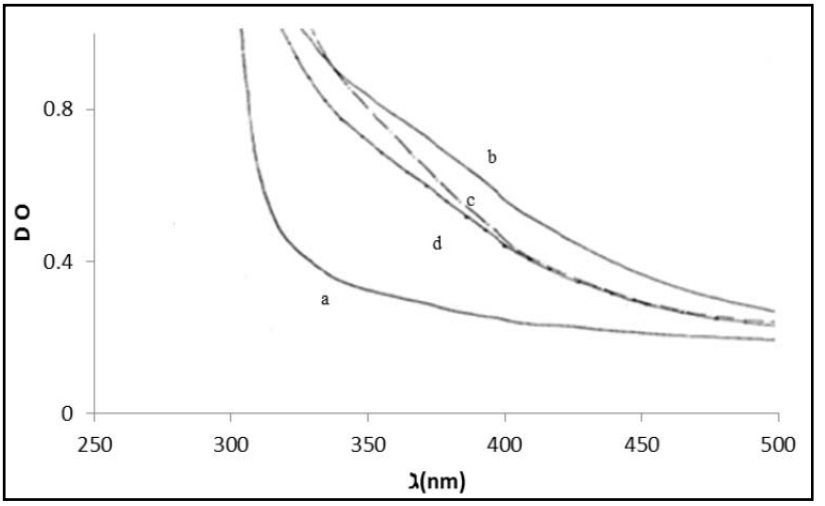


Figure 11: evolution of UV spectra of polymer UP + 50 p $CaCO_3$, irradiated under vacuum at $\lambda \geq 315$nm. (e = 148 μm)
a: initial, b: photolysis 601h at $\lambda \geq 315$nm , c: post photo-oxidation after 10h , d: post photo-oxidation after 35h

4. Conclusion

The photo-catalytic activity of Zinc sulfide and black iron oxides are much less known than those of titanium oxides and zinc oxide. With low percent, these pigments have an accelerating effect on the photo-oxidation. Moreover, the rate of photo- oxidation of polymer UP pigmented with ZnS is greater than that one observed with TiO_2, interpreted by a lower inner filter effect with ZnS.
Trends observed between 400-500 nm of the polymer UP pigmented with ZnS , are greatly different than that one of virgin samples; the concentration of absorbing photo-products is more important, due to an inner filter effect associated to this pigment .Highly absorbing and photo-chemically unstable photoproducts,especially the photolysis products ,are protected by an absorbing screen. Black iron oxides in the polymer (UP) cause an important increase of the evolution of optical density between 300-500 nm.
Added to the polymer UP, Calcium carbonate non- absorbing filler, causes a slight decrease in the evolution of the I.R. spectrum, and the protection of absorbing photo-products observed by screen diffusing effect by increasing the optical path of light; the formed photolysis products , normally photo-oxidized in the virgin polymer, are then protected. This effect of diffusing screen is as important as the rate of calcium carbonate is high.

References:

Anand Prabu, A., Alagar, M. 2004. Mechanical and thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings . *Progress in Organic Coatings*, 49: 236–243.
Avolio, R., Gentile, G., Avella, M., Carfagna, C., Errico, M. E. 2013. Polymer–filler interactions in PET/$CaCO_3$ nanocomposites: Chain ordering at the interface and physical properties, *European Polymer Journal*, 49: 419–427.
Fanton, E., Seinera, H., et Lemaire, J. 1983. Le carbonate de calcium, une charge minérale, neutre en photovieillissement des polyoléfines, *Rev. Gén. Caoutch. Plast., 60*: 57-62.

Gao, N., Li, J., Li, Z., Peng, Z. 2005. The dynamic mechanical properties of EPDMA/$Al(OH)_3$ composite, *J. Appl. Polym. Sci*., 98: 2454–2460.

Gou, Y., Su, Z., Xue, Z. 2004. Dopant effects on the photocatalytic activity of colloidal zinc sulfide semiconductor nanocrystals for the oxidation of 2-chlorophenol. *Mater. Res. Bull.,* 39: 2203–2208.
Jia, K., Pan, B.C., Zhang, Q.R., Zhang, W.M. Jiang, P.J., Hong, C.H. Pan, B.J., Zhang, Q.X. 2008. Adsorption of Pb^{2+},Zn^{2+}, and Cd^{2+} from waters by amorphous titanium phosphate, *J. Colloid Interface Sci*., 318: 160–166.

Joni, I. M., Nishiwaki, T., Okuyama K., Isoi Sh., Kuribayashi R. 2010. Enhancement of the thermal stability and mechanical properties of a PMMA/aluminum trihydroxide composite synthesized via bead milling, *Powder Technology,* 204: 145–153.

Kohtani, S., Ohama, Y., Ohno, Y., Tsuji, I., Kudo, A., Nakagaki, R. 2005. Photo reductive defluorination of hexafluorobenzene on metaldoped ZnS photocatalysts under visible light irradiation. *Chem. Lett.*, 34: 1056.
Lee, T.G., Hyun, J.E. 2006. Structural effect of the in situ generated titania on its ability to oxidize and capture the gas-phase elemental mercury. *Chemosphere*, 62: 26-33.
Lemaire, J. 1982. The Photocatalyzed Oxidation of Polyamides and Polyolefins, *Pure and Appl. Chem*., 54: 1667-1682.

Lemaire, J., Arnaud, R., Gardette, J.L., Ginhac, J.M., Tang, L., Fanton, E. 1979. Vieillissement des Polyméres: Empirisme ou Science?*, Rev. Gén. Caoutch*. *Plast.,* 593 : 147-152.

Pan, B.C., Zhang, Q.R., Du, W.,. Zhang, W.M., Pan, B.J., Zhang, Q.J., Xu, Z.W., Zhang, Q.X. 2007. Selective heavy metals removal from waters by amorphous zirconium phosphate: behavior and mechanism,*Water Research,* 41: 3103–3111.

Pardeshi, S.K., Patil, A.B. 2008. A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy. *Sol. Energy,* 82: 700–705.

Parida, K.M., Parija, S. 2006. Photocatalytic degradation of phenol under solar radiation using microwave irradiated zinc oxide. *Sol. Energy,* 80: 1048–1054.
Petruj, J., Marchal J., 1980. Mechanism of ketone formation in the thermooxidation and radiolytic oxidation of low density polyethylene, *Radiation Physics and Chemistry*, 16: 27-36.

Snider, G., Ariya, P. 2010. Photo-catalytic oxidation reaction of gaseous mercury over titanium dioxide nanoparticle surfaces. Chemical Physics Letters, 491: 23–28.

Weiss, J., Bord, C. 1983. Les matériaux composites, structure constituants fabrication. Paris , l'usine nouvelle.

Zhang, H., Chen, X., Li, Z., Kou, J., Yu, T., Zou, Z. 2007a. Preparation of sensitized ZnS and its photocatalytic activity under visible light irradiation. *J. Phys. D: Appl. Phys.*, 40: 6846–6849.
Zhang, Y.C., Chen, W.W., Hu, X.Y. 2007b. Controllable synthesis and optical properties of Zn-doped CdS nanorods from single-source molecular precursors. *Cryst. Gr*